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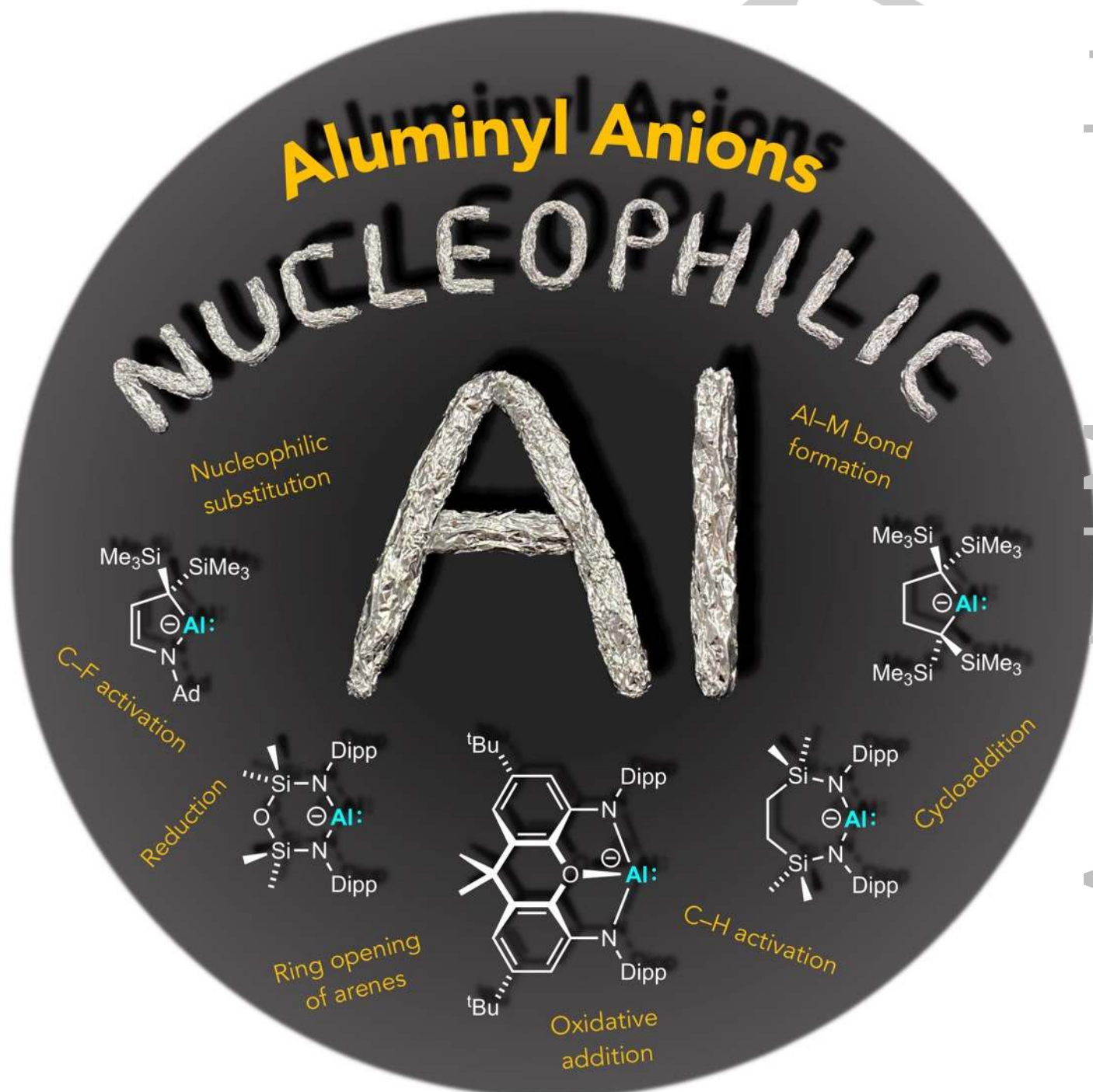
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The Aluminyl Anion: A New Generation of Aluminium Nucleophile

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Abstract: Trivalent aluminium compounds are well known for their reactivity as Lewis acids/electrophiles, a feature that is exploited in many pharmaceutical, industrial and laboratory-based reactions. Recently, a series of isolable aluminium(I) anions ('aluminyls') have been reported, which offer an alternative to this textbook description: these reagents behave as aluminium nucleophiles. This minireview covers the synthesis, structure and reactivity of aluminyl species reported to date, together with their associated metal complexes. The frontier orbitals of each of these species have been investigated using a common methodology to allow for a like-for-like comparison of their electronic structure and a means of rationalising (sometimes unprecedented) patterns of reactivity.

1. Introduction

Aluminium is the most abundant metal in the Earth's crust, accounting for >8% of its overall mass.[1] It is found in the sedimentary rock Bauxite, which is mined on a hundred million tonne scale annually. Bauxite is readily processed via the Bayer process to give alumina (Al_2O_3), the raw material for the production of aluminium metal.[2] In molecular chemistry, aluminium is most commonly found in the +3 oxidation state, with the +1 state which is favoured for the heavier Group 13 metals being strongly reducing.[3] Hence, trivalent species constitute the vast majority of aluminium compounds used in chemical synthesis, such as trialkylaluminiums (typically used as alkylating reagents) and aluminium trihalides (widely used as Lewis acids).[4] Low oxidation state aluminium compounds, i.e. those where the aluminium adopts the formal oxidation states +2, +1 or 0 are known, but are considerably less common.[5]

1.1. Aluminium(I) Complexes

Predating the work on aluminyl systems are the *neutral* aluminium compounds in the formal +1 oxidation state. The isolation of Al(I) species is challenging thermodynamically, and such species are typically highly reactive and prone to disproportionation.[6] Binary Al(I) compounds such as AlH, AlX (X = halide) and Al_2O have been reported but are only stable for prolonged periods in the gas phase at low pressures.[7] The development of cryochemical methods for the handling of metastable solutions of AlX (X = Cl, Br, I) proved to be instrumental in developing the chemistry of organo-aluminium(I) systems.[7c-f] Accordingly, the first example of an isolable aluminium(I) complex - tetrameric (AlCp*)$_4$ **1** (Figure 1, Cp* =

C_5Me_5) - was reported in 1991 by Schnöckel and co-workers,[8] from the reaction between a metastable solution of AlCl and MgCp*$_2$. An alternative synthesis using potassium metal reduction of Cp*AlCl$_2$ was later reported by Roesky and co-workers.[9] In the solid state, **1** is centred around an Al$_4$ tetrahedron capped by four η^5-Cp* ligands. The bulky Cp* ligands provide considerable kinetic stabilization, and contribute to its enhanced thermal tolerance compared to metastable AlX systems. In solution at elevated temperatures, **1** can undergo dissociation into monomeric AlCp* units, a factor which has been exploited in a significant part of its subsequently reported reaction chemistry.
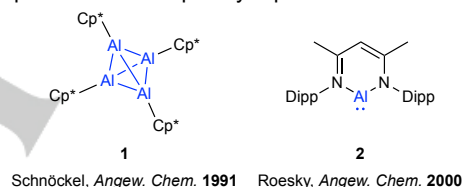
Figure 1. The first examples of isolable aluminium(I) complexes (Cp* = C_5Me_5; Dipp = 2,6-$^iPr_2C_6H_3$).

In 2000, Roesky and co-workers reported the first isolable monomeric aluminium(I) system, **2** (Figure 1), utilising a bulky *β*-diketiminate ligand.[10] **2** features a two-coordinate aluminium(I) centre and can be regarded as an aluminium analogue of an NHC, with both a lone pair and empty *p*-orbital localized on the metal centre. The reactivity of these two landmark Al(I) systems (**1** and **2**) is vast and diverse and has recently been comprehensively reviewed by Ma, Yang, Roesky and co-workers.[11] The chemistry of **2**, in particular, is undergoing a recent renaissance, being a key reagent in a number of recent publications.[12] These recent reports include the activation of small molecules (CO, C_2H_4)[12 c,j], reduction chemistry (including that of benzene),[12b,e,l,k,m] cycloadditions[12a,d,g] and various bond activations including (C–H and C–F).[12 c,f,h,l,n] The vast majority of the reactions of **1** and **2** are best described oxidative additions, although some evidence of nucleophilic behaviour has been reported (especially with electropositive metals/Lewis acids) and this has been exploited in the formation of Al–metal donor/acceptor bonds.[11] Since the initial reports of **1** and **2**, various other neutral aluminium(I) systems have been reported using an array of bulky ligands. These include the remarkable NHC-stabilised dialumene reported by Inoue and co-workers,[13] the cyclic alkyl amino carbene (CAAC) supported Al(I) hydride complex[14] and the monomeric ^{tBu3}CpAl(I)[15] reported by Braunschweig and co-workers and as well as a number of other Al(I) tetramers supported by bulky ancillary ligands.[3,5]

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Simon Aldridge is originally from Shrewsbury (UK) and is Professor of Chemistry at the University of Oxford, and Director of the EPSRC/Oxford Centre for Doctoral Training in Inorganic Chemistry for Future Manufacturing. He has published more than 210 papers and is a past winner of the RSC's Main Group Chemistry (2010) and Frankland Awards (2018). His research interests include the development of p-block compounds with unusual electronic structure, and their applications in small molecule activation and catalysis.

1.2. Anionic Group 13 Centred Nucleophiles

Before our initial report of an anionic aluminium(I) complex (an 'aluminyl' anion)[16] in 2018, analogous anions of the other group 13 elements, including boron, gallium and indium were already known in the literature. The first of these to be reported

was the gallyl anion, $[(^{tBu}DAB)Ga]^-$ **3** ($^{tBu}DAB = [(^{t}BuNCH)_2]^{2-}$) by Schmidbaur and co-workers over 20 years ago (Figure 2).[17] This was followed by a diaryl substituted version reported by Jones and co-workers in 2002[18a] and a BIAN stabilised version in 2008 by Fedushkin, Schumann and co-workers.[18b] The reactivity of these gallyl anions have been thoroughly investigated, especially with regards to their coordination chemistry.[19] However, very little has been reported with respect to small molecule activation with these systems.
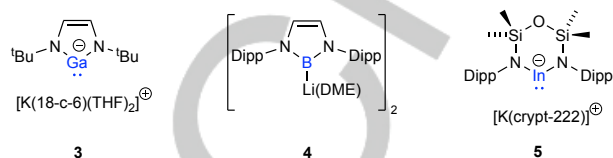
3
Schmidbaur, *JACS* **1999**

4
Yamashita, Nozaki, *Science* **2006**

5
Coles, *Angew. Chem.* **2018**

Figure 2. The first reported gallyl, boryl and indyl anions (18-c-6 = 18-crown-6; crypt-222 = cryptand 222)

In 2006, Yamashita and Nozaki reported the groundbreaking boryl lithium complex, $[(^{Dipp}DAB)BLi(DME)]_2$ **4** ($^{Dipp}DAB = [(DippNCH)_2]^{2-}$), the first isolated example of a boryl anion (Figure 2).[20] Unlike the potassium gallyl **3**, which was initially isolated as an ion separated pair, **4** shows a strong electrostatic interaction between the boron lone pair and the lithium cation. Boryl system **4** exists as a dimer in the solid state (with two DME molecules bridging the two Li^+ cations), however a monomeric version of this complex has since been reported.[21] To date, boryl anions featuring an array of chelating ligands have been reported,[22,23] all of which exhibit strong interactions between the boron and the cation (either covalent or electrostatic); no charge-separated boryl anion has yet been reported.

The reactivity of the boryl anions has become an area of considerable interest over the last decade. They have been shown to be highly reactive reagents, which is partly due to their relatively small HOMO-LUMO energy gap. This defining feature allows them to activate a wide array of small molecules and/or substrates with strong σ- and π-bonds. In addition, their highly directional lone pair also makes them ideal ligands in coordination chemistry. The reactivity of boryl anions has recently been covered in a comprehensive review by Weber.[22]

The heaviest member of the known group 13 element(I) anions is the indyl anion. Currently, only one example of an indyl anion is known, which was reported by Coles and co-workers in 2018.[24] The anion was reported as both an ion separated pair **5** (Figure 2) and as the more tightly bound lithium complex. Little reactivity of this indyl compound has yet been reported. However, preliminary studies with MeOTf and bulky metal halide complexes suggest nucleophilic behaviour,[24] whilst reactions with organic azides lead to oxidation of the indium.[25]

2. Aluminyl Anions

2.1. Synthesis and Structure

Since the isolation of gallyl compound **3** in 1999, various research groups have targeted an aluminium analogue, in particular using similar diazabutadiene supporting ligands. In

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2002, Jones and co-workers reported the reduction of (Dipp DAB)AlI$_2$ with potassium metal.[18a] This reaction, however, generates (Dipp DAB)H$_2$ and aluminium metal. The groups of Graves, Mair and Yang also reported reductions of similar diazabutadiene ligated aluminium halide complexes but no signs of an aluminyl anion were mentioned in any of these reports.[26]

2.1.1 Diamido Aluminyl Systems

In 2018, we reported an aluminyl anion, K$_2$[Al(NON)]$_2$, **6**, stabilised by the bulky xanthene-based diamido ligand [NON]$^{2-}$ (Figure 3).[27] **6** was prepared by the two-electron reduction of the neutral Al(III) precursor complex (NON)AlI with excess KC$_8$. Interestingly, adding the reducing agent in the correct stoichiometry (i.e. 2 equiv. of KC$_8$) was found to give large amounts of the dialumane [(NON)Al]$_2$, presumably by the radical coupling of two (NON)Al· units and/or by nucleophilic attack of the of the aluminyl on the (NON)AlI starting material (see section 2.3.). In contrast to the digallane [(tBuDAB)Ga]$_2$ (which is readily reduced by potassium metal to give potassium gallyl complex **3**),[17] [(NON)Al]$_2$ does not react with potassium (or KC$_8$) even at elevated temperatures. This suggests the synthesis of **6** does not go through the dialumane as an intermediate in the reaction.
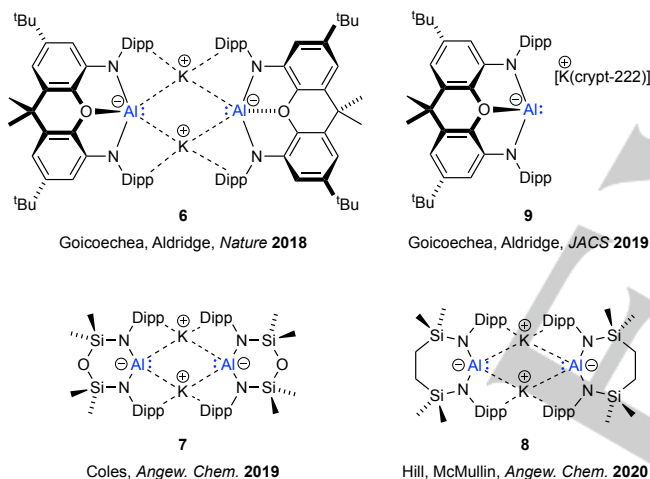

Figure 3. Structures of the diamido substituted aluminyl anion complexes **6-9**.

The structure of **6** was confirmed by X-ray crystallography, which revealed the complex to exists as a dimer in the solid state. The dimer is held together by interactions between the flanking aryl groups on the NON ligands and the potassium cations. The aluminium centres are >6.6 Å apart, implying no significant interaction between them. It can also be shown by DOSY NMR experiments that the dimeric structure of **6** is retained in solution.[27] In **6**, there is a (relatively weak) interaction between the O atom incorporated into the backbone of the NON ligand and the aluminium centre (2.28 Å).[27]

Subsequently, two further potassium aluminyl complexes featuring bidentate diamido ligands have been reported.[28] The first of these, K$_2$[Al(^{Si}NON)]$_2$ (**7**), was reported by Coles and co-workers in 2019,[29] and more recently K$_2$[Al(NCCN)]$_2$ (**8**) was reported by Hill, McMullin and co-workers in 2020 (Figure 3).[30] Both of these complexes were synthesised using a similar synthetic route to **6**, i.e. by the two-electron reduction of the corresponding aluminium(III) iodide precursor with potassium.

Superficially, both **7** and **8** possess similar structures to **6**: both are dimeric in the solid state featuring interactions between the flanking aryl rings of the bulky diamido ligands and the potassium cations. **7** features a 6-membered aluminium-containing heterocycle, with a N-Al-N angle of 103.89(8)°,[29] while the 7-membered ring in **8** (not surprisingly) makes the corresponding unit somewhat wider (108.84(9)°).[30] Both of these angles however are considerably smaller than that in **6** (128.11(9)°).[27]

To date, only two examples of truly 'naked' aluminyl anions have been reported, i.e. aluminyl anions that show no significant interaction with the cation. The first of these is the charge-separated complex [K(crypt-222)][Al(NON)] **9** (Figure 3), reported by us in 2019.[31] The second example is complex **11** discussed below. Complex **9** is prepared in straightforward fashion by the addition of cryptand-222 to **6** in THF. The solid-state structure of **9** confirms that the K$^+$ cations are encapsulated within the cryptand, and that the [Al(NON)]$^-$ anion engages in no close interactions with the cation (all K···Al interactions >7 Å).

2.1.2. Alkyl Aluminyl Systems

Other than the series of diamido supported aluminyl anions discussed above, two further examples of aluminyl anions have recently been reported. These are the remarkable alkyl substituted aluminyl complexes [K(toluene)$_2$–Al{(C(SiMe$_3$)$_2$CH$_2$)$_2$}] **10** and [K(12-crown-4)$_2$][Al(CAA)] **11** (CAA = cyclic alkyl amino), both reported earlier this year by the groups of Yamashita and Kinjo, respectively (Figure 4).[31,32] Unlike the diamido supported aluminyl complexes **6-8**, which were all synthesised by reduction from their corresponding Al(III) iodide complexes, **10** and **11** were both synthesised by reduction of the corresponding Al-Al bonded dialumanes. This contrasts with the synthesis of **6**, for which reduction of the dialumane [(NON)Al]$_2$ is not possible (at least under conditions that the aluminyl is stable).[27]
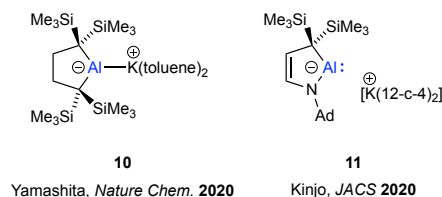
Figure 4. Structures of alkyl substituted aluminyl complexes (12-c-4 = 12-crown-4).

The structures of **10** and **11** have been determined by X-ray crystallography and are monomeric in the solid state. Both feature 5-membered aluminium heterocycles, with similar C–Al–R angles (R = C, **10**; N, **11**); **11** being the slightly more acute at 86.8(1) compared with 90.40(5)° for that in **10**.[32,33] In the solid state, aluminyl **10** shows a significant interaction between the aluminium centre and the potassium cation (Al–K 3.4549(5) Å). However, the Al–K distance is considerably longer than the sum of the covalent radii of Al and K (3.24 Å)[34] suggesting an electrostatic interaction between the Al lone pair and cation, similar to that observed in boryl lithium **4**.[20] Attempts were made by the authors to synthesise a charge separated analogue by the addition of cryptand-222 or THF to **10**. However, both of these reactions led to immediate decomposition of the aluminyl anion.[32] Compound **11** on the other

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hand is a *bone fide* charge-separated species, and only the second reported example of a 'naked' aluminyl anion. The K$^+$ cation in **11** is contained within two 12-crown-4 ligands and consequently has no close interactions with the aluminyl fragment (closest Al···K distance >6.6 Å).[33]

2.2. Electronic Structure

For the purposes of like-for-like comparison, the electronic structures of all of the known aluminyl anions have been assessed by quantum chemical methods using the same level of theory as part of the present review (DFT-D3, PBE0, Def-TZVP – see SI for details). The calculations have been performed on the (full) monomeric anions, neglecting any stabilising/destabilising interactions with the counter-cations, and are summarised in Figure 5. All five anions possess relatively similar HOMO-LUMO energy gaps, varying by <0.3 eV (approx. 25 kJ mol^{-1}). More important in terms of reactivity is the energy separation between the occupied and vacant orbitals at the aluminium centre (i.e. the lone pair of electrons and the empty p_z-orbital). In all cases, the HOMO corresponds to a lone pair on aluminium. However, in every case bar the anionic component of **10**, the LUMO is a ligand-based orbital, with the empty Al p_z-orbital being higher in the orbital manifold: the LUMO+3 for the three diamido systems **6-8** and the LUMO+1 in **11** (see SI for more information). That said, the energy gap between the HOMO and the LUMO+n (LUMO+n corresponding to the empty Al centred p-orbital) is also similar in all cases, varying by a maximum of just over 50 kJ mol^{-1} (from 3.42 eV, 330 kJ mol^{-1} for **10** to 4.06 eV, 392 kJ mol^{-1} for **7**).
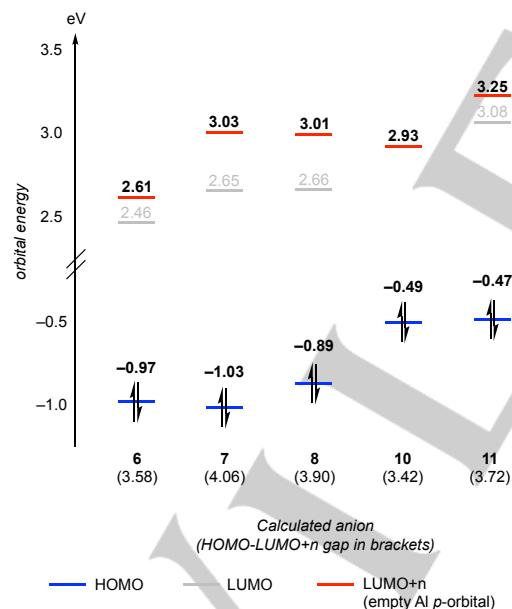
Figure 5. Calculated HOMO, LUMO and LUMO+n energies of reported aluminyl anions at the DFT-D3, PBE0, Def-TZVP level of theory (LUMO+n indicates the orbital associated with the aluminium empty p-orbital). Orbital energies displayed in eV.

In general terms, many of the energetic trends shown in Figure 5 can be ascribed to structural factors familiar from carbene chemistry.[35] Thus, the lower lying nature of the HOMO

for diamido systems **6**, **7** and **8** compared to **10** and **11** (which feature alkyl substituents) can be ascribed to the more electronegative nature of the α-substituent. That the HOMO energies for **10** and **11** are so similar despite the narrower angle at aluminium and the presence of one σ electron-withdrawing nitrogen substituent in the latter is perhaps more surprising. The diamido aluminyl systems **7** and **8** are structurally very similar, with a slight difference being the wider N–Al–N angle in **8**, consistent with the larger heterocycle size (108.84(9)° *cf.* 103.89(8)° for **7**). As such, the HOMO energy is marginally higher in the case of **8** (by 14 kJ mol^{-1}), consistent with higher p-character. Interestingly, however, the HOMO of **6**, which features both a much wider N–Al–N angle (128.1(1)°) and potentially a weak additional donor/acceptor interaction from the xanthene oxygen is in a similar energy range.

In terms of the unoccupied orbitals, the differences between **10** and **11** also conform to established trends in carbene chemistry. Anion **10** is the only system where the Al p_z-orbital contributes to the LUMO; the analogous orbital in **11** is the LUMO+1. The difference in energy between these two orbitals is >30 kJ mol^{-1}, with that of **11** being the higher of the two, consistent with π-donation from the single amido substituent. For the diamido aluminyl systems **6-8**, the orbital characterized by significant Al p_z character lies higher in the orbital manifold (LUMO+3 in each case), with systems **7** and **8** being associated with almost identical energies. Superficially, the most surprising finding is the much lower lying nature of the corresponding orbital for xanthene-derived system **6**. On the face of it, this would imply relatively little elevation on the basis of Al-O σ* character, and most significantly, much reduced N-to-Al π donation from the amido substituents (*cf.* **7** and **8**, see SI for molecular orbital images). The underlying origins for this are geometric in nature, and find precedent in the anti-Bredt carbene systems reported by Bertrand and co-workers.[36] In marked contrast to **7** and **8**, the amido substituents in **6** do not lie coplanar with the AlN$_2$ unit (Figure 6). The X-ray crystal structures of both dimeric K$_2$[Al(NON)]$_2$ and monomeric [K(2.2.2-crypt)][Al(NON)] reveal that the angles between the AlN$_2$ and NC$_2$ planes in these systems are typically of the order of 40-55° (e.g. 53.7 and 50.9° for [K(2.2.2-crypt)][Al(NON)]). Geometrically, this relates to the 'folded' non-planar geometry of the xanthene backbone required to accommodate the aluminium centre between two substituents in the 4- and 5-positions. As such, N-to-Al π-donation is severely restricted, as reflected in the significantly longer Al-N bonds measured for **6** compared to those in **7** and **8** (e.g. 2.022(1)/2.049(1) Å for [K(2.2.2-crypt)][Al(NON)], *cf.* 1.879(2)-1.896(2) Å for **7**).
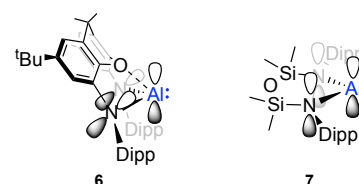
Figure 6. Diagrammatic representation of the orbitals involved in the N-to-Al π-donation for anions **6** and **7**.

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In summary, dialkylaluminyl compound **10**, not unexpectedly features the smallest energy gap between the HOMO and the Al p_z-orbital at (3.42 eV, 330 kJ mol^{-1}). The corresponding energy separation for alkyl amino aluminyl **11** is higher (3.72 eV, 360 kJ mol^{-1}) due to elevation of the Al p_z-orbital, while those for the planar diamido systems **7** and **8** are higher still. Anion **7** features the largest energy separation (4.02 eV, 392 kJ mol^{-1}) with that of the related 7-membered system **8** being slightly smaller (3.90 eV, 376 kJ mol^{-1}) due to the effects of ring expansion on the HOMO. 'Base-stabilized' system **6** appears in reality to be destabilized by the constraints of the xanthene ligand backbone (with a corresponding energy separation of only 3.57 eV, 345 kJ mol^{-1}) due to geometrically restricted N-to-Al π donation. In terms of understanding reactivity patterns, it should be noted that only compounds **6** and **11** have so far been isolated as 'naked' aluminyl anions. For ion pairs, interaction between the Al lone pair and the K$^+$ cation would be expected to stabilise the HOMO and thereby widen the respective energy gaps.

2.3. Reactivity

2.3.1 Nucleophilic Substitution

One of the foremost points of novelty of aluminyl anions is their ability to react as aluminium-centred nucleophiles. All of the reported aluminyl anions have shown nucleophilic behaviour to some extent, with **6**, **8** and **10** showing evidence for nucleophilic substitution chemistry.[27,30,32,37,38]

In our initial report we showed that **6** could undergo nucleophilic substitution reactions with carbon- and metal-centred electrophiles, as well as with a proton source.[27] The reaction of **6** with either MeI or MeOTf in toluene leads to an almost instantaneous reaction to give the Al–C bonded complex (NON)AlMe **12** with elimination of corresponding potassium salt (Scheme 1). Yamashita and co-workers have reported a similar reaction between **10** and MeOTf, yielding the aluminium methyl complex **13**.[32] Both of these complexes were synthesised by nucleophilic attack on the electrophilic carbon centre of MeI or MeOTf by the aluminyl. We also showed that a similar reaction can be performed using a bulky weak acid such as H$_2$(NON). This leads to formal nucleophilic attack on a proton (i.e. protonation) to give the aluminium hydride **14** (Scheme 1).
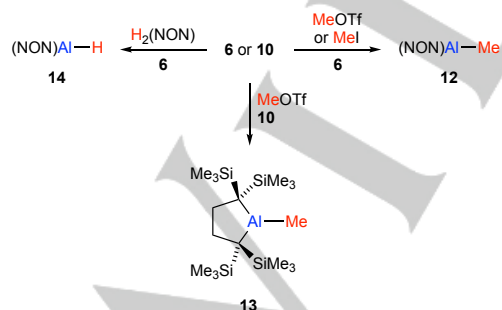
Scheme 1. Nucleophilic substitution reactions of **6** and **10** with carbon and hydrogen electrophiles.

Nucleophilic substitution reactions have also been successfully employed in the synthesis of a range of Al–metal covalent bonds.[27,30,37,38] This was first demonstrated in reactions between **6** and bulky Mg/Al iodide electrophiles,[27] which were

used to generate the corresponding Al–Al and Al–Mg bonded complexes **15** and **16** (Scheme 2). A small number of additional Al–metal bonded complexes have since been synthesised by this route, including those with Al–Ca (**18**)[30] and Al–Y (**19**)[38] Al–Au (**20** and **21**)[37] bonds (Scheme 2). It is noteworthy that all of these nucleophilic substitution reactions use electrophiles featuring weakly coordinating anions (i.e. OTf$^-$, I$^-$, BPh$_4$$^-$), in order to promote salt elimination. Attempting these reactions with more coordinating anions (e.g. F$^-$ or Cl$^-$) tends to lead to the formation of 'ate' complexes (i.e. formal oxidative addition products) with the anion bound to the Al centre (see 2.3.2).
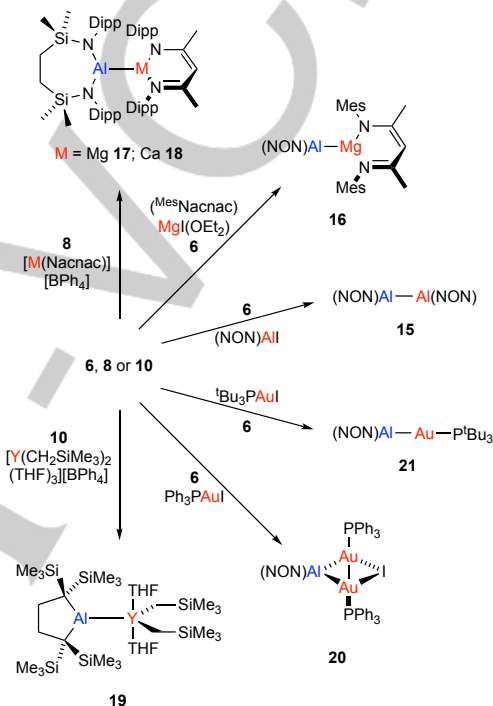
Scheme 2. Nucleophilic substitution reactions of aluminyl anions to form the Al–metal bonded complexes **15-21**.

The Al–metal bonded heterobimetallic products **16-21** have also shown some interesting reactivity. These complexes can generally be divided into two groups depending on the polarisation of the Al–metal bond. If the aluminium centre is bound to a metal with an electronegativity lower than itself (i.e. <1.61 on the Pauling scale), then (superficially) the compound would be expected to be polarized in the sense Al(δ–)-M(δ+), with the reactivity profile of an aluminium-centred nucleophile (albeit moderated by the degree of polarity in the M-Al bond). At the other end of the spectrum, if aluminium is bound to a metal with an electronegativity greater than itself, then polarization would be expected in the sense Al(δ+)-M(δ–), consistent with a description as an aluminium electrophile bound to an electron-rich metal centre. Magnesium, calcium and yttrium all have electronegativities <1.61, and **16-19** might therefore be regarded as coordinated aluminyl complexes.[27,30,38] No reactivity of **16** or **19** has yet been reported, however unpublished work from our laboratory shows that **16** does in fact react as an aluminium centred nucleophile with various electrophiles including MeI. Reports on compounds **17** and **18** state that neither compound displays any observable reaction with benzene or toluene. **18** has been shown to react with both THF and cyclooctatetraene (COT);

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17 on the other hand shows no reactivity towards either of these substrates.[30]

In contrast, gold has an electronegativity considerably greater than that of aluminium (2.54 on the Pauling scale). Accordingly, the Al–Au bonds in **20** and **21** show reversed polarization compared with the Al–metal bonds in **16-19**.[37] Reactions of **21** with the carbon centred electrophiles CO_2 and diisopropylcarbodiimide yield isolable Au–C bonded products. These reactions constitute the first examples of nucleophilic attack by a stable molecular gold complex.

2.3.2 Oxidative addition

As previously demonstrated for neutral Al(I) systems, the two-electron oxidation of Al(I) to Al(III) is typically a highly thermodynamically favourable process.[11] The situation appears to be little different for anionic aluminyl ions. As such, various oxidative addition reactions have been reported for aluminyl systems, in some cases involving the cleavage of very strong σ-bonds.[27,31-33]
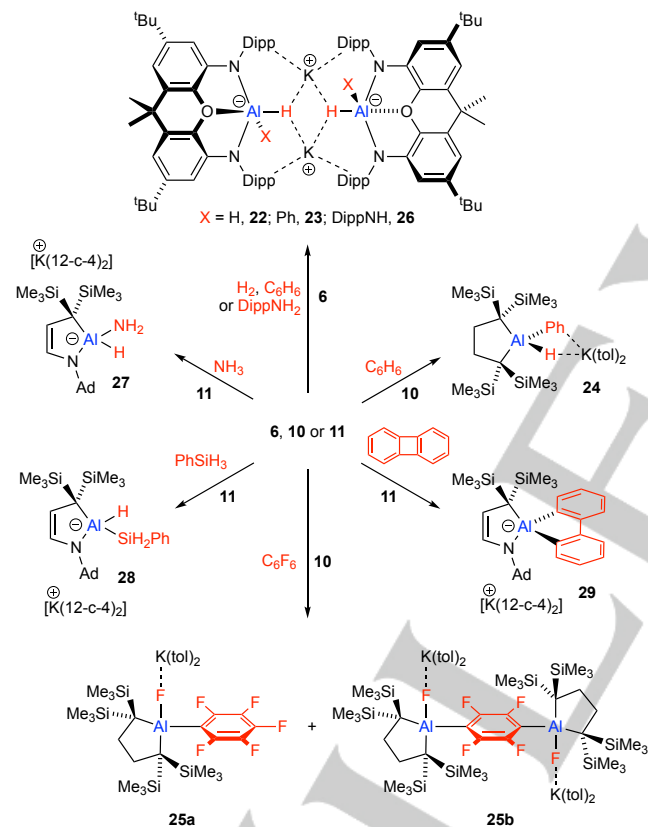
Scheme 3. Oxidative addition reactions of aluminyl anions **6**, **10** and **11**; tol = toluene.

In our initial work, we showed that **6** can oxidatively cleave the H–H bond of H_2 and a C–H bond in benzene under mild reaction conditions.[27] These reactions generate the formal oxidative addition products **22** and **23** (Scheme 3), demonstrating that the activation of strong σ-bonds by aluminyl anions is achievable. Furthermore, the reaction to yield **23** represented the first example of the oxidative addition of a benzene C–H bond at a single well-defined main-group metal centre. In more recent

work, we also showed that C–H activation of naphthalene was also possible.[31]

Since then, Yamashita and co-workers have shown that **10** can also C–H activate benzene at room temperature (RT) to give the formal oxidative addition product **24** (Scheme 3).[32] The same group also reported reactions of **10** with C_6F_6 and benzyl chloride. The reaction with C_6F_6 yields a mixture of formal oxidative addition products **25a** and **25b**, showing mono- and di- activation of the C_6F_6, respectively. The ratio of these products was shown to vary depending on the molar ratio of C_6F_6 used. In contrast, the reaction of **10** with benzyl chloride did not give the expected C–Cl oxidative addition product, but a mixture of the corresponding benzylaluminate and chloroalumane. This result suggests that **10** is susceptible to a nucleophilic substitution at the chlorine atom that generates the chloroalumane and benzylpotassium.[32]

Earlier this year, we showed that the activation of N–H bonds by an aluminyl anion was also possible, with the reaction between **6** and $DippNH_2$. This reaction gave the corresponding oxidative addition product **26** (Scheme 3).[39] Kinjo and co-workers followed this report by demonstrating that the N–H activation of ammonia and Si–H activation of phenylsilane are also possible with **11**.[33] These reactions led to the formal oxidative addition products **27** and **28** (Scheme 3). The group also showed reactivity with borane in the construction of an σ-aromatic AlB_2 ring and cleavage of a strained C–C bond in biphenylene to give the ring opened product **29**. The latter is the second example of C–C bond activation by a potassium aluminyl complex. The first reported C–C bond activation by an aluminyl anion was the remarkable ring opening of benzene reported by us in 2019.[31] The 'naked' aluminyl **9** reacts cleanly with benzene at RT to give the 7-membered aluminium heterocycle **30** in high yields (Scheme 4). This reaction involves the oxidative cleavage of a C–C bond in benzene at a single aluminium centre. Remarkably, this reaction was also found to be reversible when heated. The ring opening of benzene to give **30** was calculated to be energetically favourable (-17 kJ mol^{-1}), even taking into account the loss of aromaticity in benzene.[31] This has since been confirmed in a more comprehensive computational study by Fernández and co-workers reported earlier this year,[40] where the authors also investigated the effects incorporating electron withdrawing groups (EWGs) onto the ring and the C–C activation of the polycyclic aromatic systems naphthalene and anthracene. The study found that C–C activation of the polycyclic systems was unlikely, as the competing C–H activation pathway had a lower activation barrier (and more energetically favoured products). On the other hand, incorporating EWGs onto the benzene was found to favour the C–C activation both kinetically (by lowering the activation barrier) and thermodynamically. Unfortunately, this would be difficult to confirm experimentally as **9** would likely react with most of the common EWGs. Haloarenes, for example, are known to react with the related dimeric system **6** via formal C-I oxidative addition.

**Scheme 4.** Ring opening of benzene by the monomeric aluminyl anion **9**.

Compound **30** was found to react with 2 equivalents of the electrophile Me_2SnCl_2, yielding the *cis,cis,cis*-triene **31** and the

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corresponding dichloroaluminate.[31] This reaction ultimately shows that aluminyl anions can be used to generate functionalized acyclic products from aromatic molecules.

2.3.3 Cycloaddition

Various cycloaddition reactions have been reported for aluminyl anions, including those with alkenes, alkynes and polyaromatics.[29,31,41] The first of these to be reported was the reaction between **7** and cyclooctatriene (COT) by Coles and co-workers.[29] This reaction led to the two-electron reduction of the COT molecule to the essentially planar aromatic anion [COT]$^{2-}$ dianion, which engages in η^2-coordination to the Al centre in the product (**32**; Scheme 5). The addition of 18-crown-6 to this complex leads to its conversion to **33**, the product of a formal (1+4) cycloaddition addition product of COT to the aluminium centre (Scheme 5). Last year, we also reported that **6** can perform cycloaddition reactions, in this case with ethylene under slightly elevated pressure (2 bar).[31] This gave the (1+2) cyclised product **34** (Scheme 5).
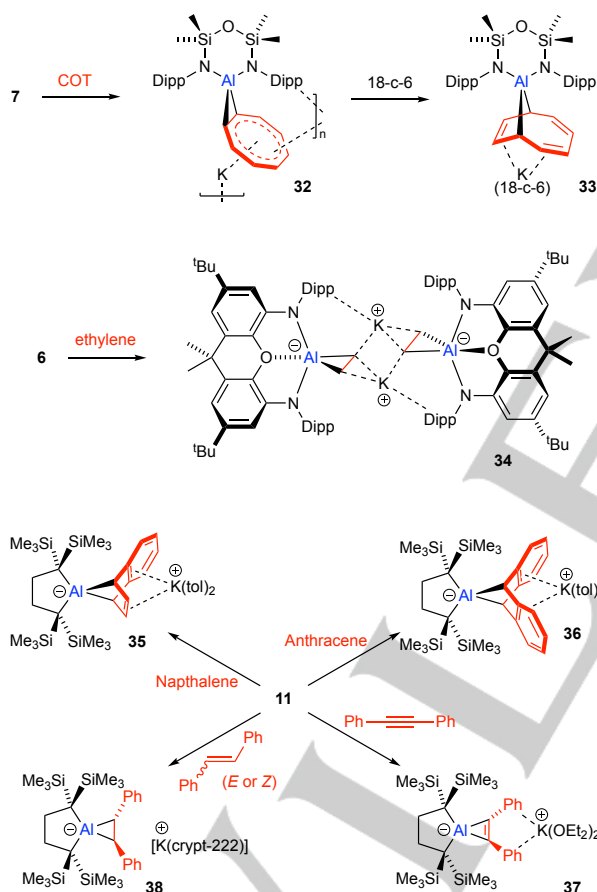
Scheme 5. Cycloaddition reactions between aluminyl anions **6**, **7** and **11** and various unsaturated substrates.

The most detailed study on cycloaddition reactions involving an aluminyl anion was reported earlier this year by Yamashita and co-workers.[41] In this report, the authors showed that **11** can undergo various cycloaddition reactions with naphthalene **35**, anthracene **36**, diphenylacetylene **37** and 1,2-stilbene **38** (both *E* and *Z*). Compound **11** reacts with the polycyclic aromatic systems naphthalene and anthracene via a (1+4) cyclisation reaction at RT,

giving the aluma-norbornadiene derivatives **35** and **36**, respectively (Scheme 5). Interestingly **6** also undergoes a (1+4) cycloaddition reaction with naphthalene at RT, but at 80 °C yields C-H activation products,[31] suggesting that the cycloaddition products of this type are kinetic products. Aluminyl complex **11** also undergoes (1+2) cycloaddition reactions with diphenylacetylene and (E)/(Z)-stilbenes, forming products **37** and **38** featuring AlC$_2$ 3-membered rings (Scheme 5). Interestingly, the reactions of **11** with both (*E*)- and (*Z*)-stilbenes gave exclusively the *trans*-cycloadduct **38**. DFT calculations revealed that the cycloaddition of **11** with (*Z*)-stilbene proceeds via a single transition state with a carbanion character, which results in the selectivity towards the *trans*-cycloadduct.[41]

2.3.4. Oxidation

Considering the highly reducing nature of the aluminyl anions, it comes as no surprise that these systems have been shown to react with a range of oxidising agents. However, by reversing the 'normal' reactivity of aluminium from electrophilic to nucleophilic, a range of previously inaccessible (in some cases highly reactive) Al(III) complexes can be accessed via this route.

In 2019, Coles and co-workers synthesised aluminium analogues of carbonyl and dioxirane moieties by oxidation with selenium.[42] The 1:1 reaction between **7** and elemental selenium (using a catalytic amount of tri-*n*-butylphosphine) gave the aluminium selenide complex **39** in moderate yield (Scheme 6). The complex was found to be highly insoluble in common organic solvents due to an extended network of interactions between the potassium cation and the selenide and aryl groups in the solid state. This network could be broken with the addition of cryptand-222 to sequester the potassium cations to give a soluble monomeric form, **40** (Scheme 6). Complexes **39** and **40** represent the first examples of aluminium-selenium carbonyl analogues. DFT analysis performed on **40** found a Wiberg bond index of 1.39 for the Al–Se bond, implying significant multiple bond character, even though it is highly polarized.[42] Addition of a further equivalent of selenium to **40** in THF yields complex **41**, which features an AlSe$_2$ three-membered ring (Scheme 6), which can be viewed as a heavy dioxirane analogue. The synthesis of **41** was also reported in a single step reaction by the addition of **7** to a suspension of selenium (2 equiv.) and cryptand-222 in THF. In a more recent account,[43] the group also reported the oxidation of **7** with sulphur, targeting the sulphur analogue of **39**. This reaction however did not give the targeted monosufide but the 5-membered AlS$_4$ ring **42**.
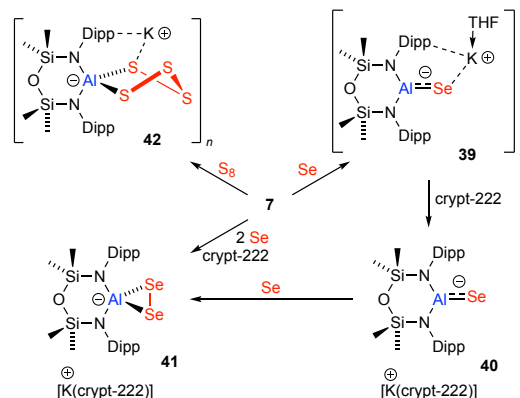
Scheme 6. Oxidation of **7** with chalcogens.

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Later in 2019, two reports emerged almost simultaneously describing the reactivity of aluminyl anions with CO_2 and N_2O. These reports were by ourselves[44] and by Anker and Coles.[45] In our report,[44] we showed that **6** reacts rapidly with 1 atm. of CO_2 at RT, cleanly yielding the aluminium carbonate species **43** (Scheme 7). We also reported the analogous reaction between **6** and the phenyl isocyanate, which gave the isoelectronic aluminium carbamate complex **44**. Both reactions were shown to proceed via a two-step mechanism; first by initial reduction of the substrate (to give CO or PhNC) and a highly reactive aluminium oxide intermediate, which undergoes a (2+2) cycloaddition with a second equivalent of the substrate to yield the isolated products **43** and **44**. Similar reactions have been reported with other low oxidation state main group systems.[46] In an attempt to isolate the oxide intermediate, the oxidation of **6** with N_2O was investigated. However, the reaction between **6** and N_2O (1 atm.) in toluene did not give the targeted oxide species, but the rather unexpected *cis*-hyponitrite complex **45**. As with the syntheses of **43** and **44**, the reaction seems to proceed via a highly reactive oxide intermediate, which remarkably undergoes a (2+3) cycloaddition with a molecule of N_2O. This reaction demonstrates the first example of a *cis*-hyponitrite ligand being directly synthesised from N_2O. The reaction between **6** and N_2O in toluene was monitored by low temp. ^1H NMR, but even at –80 °C, no signs of an intermediate were observed. However, it was found that the intermediate could be trapped by the coordination of THF to the Al centre, by performing the reaction in THF at low temperature The reaction between **6** and N_2O (1 atm.) <0 °C cleanly gives the THF-coordinated monoaluminoxane **46** in high yield (Scheme 7).[44]
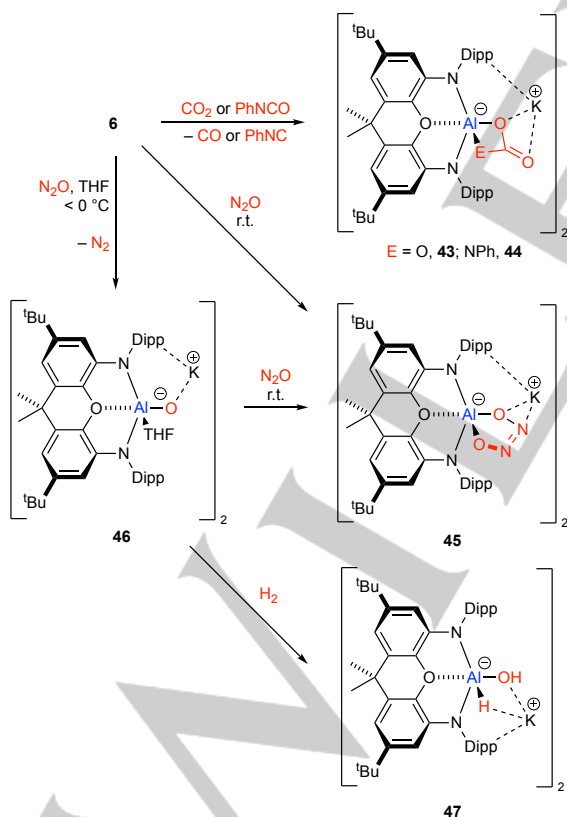
Complex **46** was found to be stable in the solid state at RT but not in solution, decomposing over the course of several hours. **46** was found to react with CO_2, PhNCO and N_2O at RT to give the previously isolated products **43-45**, showing that the (more reactive) base-free monoaluminoxane is a viable intermediate in these reactions. Remarkably, we also found that due to the extremely polar Al–O bond, **46** could heterolytically cleave H_2 at RT to give the aluminium hydride/hydroxide species **47** (Scheme 7).

Anker and Coles reported a similar study,[45] showing that aluminyl **7** also reacts with 1 atm. of CO_2 to give the aluminium carbonate complex **48** (Scheme 8). However, in their case, they found that the monoaluminoxane intermediate **49** could be isolated without the coordination of a Lewis-base, directly from the reaction of **7** and N_2O (1 atm.). In an analogous fashion to **46**, the monoaluminoxane **49** was found to react with CO_2 and N_2O (in the presence of cryptand-222) in cycloaddition reactions to give **42** and the *cis*-hyponitrite complex **50**. Addition of cryptand-222 to **49** in the absence of CO_2 or N_2O, leads to intramolecular C–H activation of the ligand across the Al–O bond; C–H activation has not yet been reported for **46**.
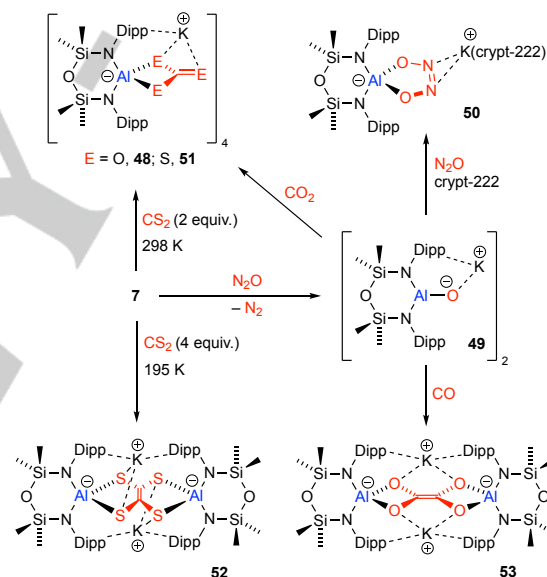
Scheme 8. Oxidation of **7** with CO_2 and N_2O and subsequent reactivity of monoaluminoxane **49**.

In a more recent account,[43] the Coles group showed that an aluminium trithiocarbonate complex **51** (Scheme 8) could also be synthesised, by the addition of a hexane solution of **7** to a solution of CS_2 (2 equiv.) at RT. However, in this case the expected monosulfide intermediate could not be isolated (see Scheme 6). Interestingly though, the group found that performing the same reaction under slightly different conditions (4 equiv. 195 K), a different product could be isolated. This was the ethenetetrathiolate complex **52** (Scheme 8), which is synthesised by a C–C bond forming reaction between two CS_2 units. Remarkably, the synthesis of the lighter analogue, the ethenetetraolate complex **53** was also reported, by the reaction between CO and the monoaluminoxane **49**. This complex represents the first report of an ethenetetraolate ligand.

Scheme 7. Oxidation of **6** with CO_2, PhNCO and N_2O and subsequent reactivity of monoaluminoxane **46**.

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The oxidation of **6** and **7** have also been investigated with regards to organic azides.[39,47] Two recent reports have found that under certain conditions, these reactions can give isolable aluminium imide complexes with highly polarised (and highly reactive) Al–N bonds. Earlier this year, our group reported reactions of **6** with various azides using a variety of reaction conditions (Scheme 9).[39] The RT reaction between **6** and 2 equiv. of trimethylsilyl azide gave the aluminium tetrazine complex **54**, which is essentially isostructural to the *cis*-hyponitrite complex **45**.[44] It can be proposed that the reaction to give **54** proceeds via a similar mechanism to that to give **45**; i.e. firstly by reduction of one molecule of azide to give a highly reactive aluminium imide intermediate, which undergoes a (2+3) cycloaddition reaction with a further equivalent of the azide to give **54**. In an attempt to trap this azide intermediate, the 1:1 reaction between **6** and trimethylsilylazide was attempted in toluene at –80 °C. This did not give the targeted imide but instead the C–H activated toluene product **55** (Scheme 9), demonstrating the highly basic nature of the aluminium imide intermediate. In an attempt to isolate a stable aluminium imide, the bulkier azide DippN₃ was sought. In a 1:1 reaction between **6** and DippN₃, the targeted aluminium imide **56** was isolated in high yields (Scheme 9). The compound was found to feature an extremely polar Al–N bond (Mulliken charges +0.67 Al and –0.16 N) with a Wiberg Bond Index (WBI) of 0.705.[39]
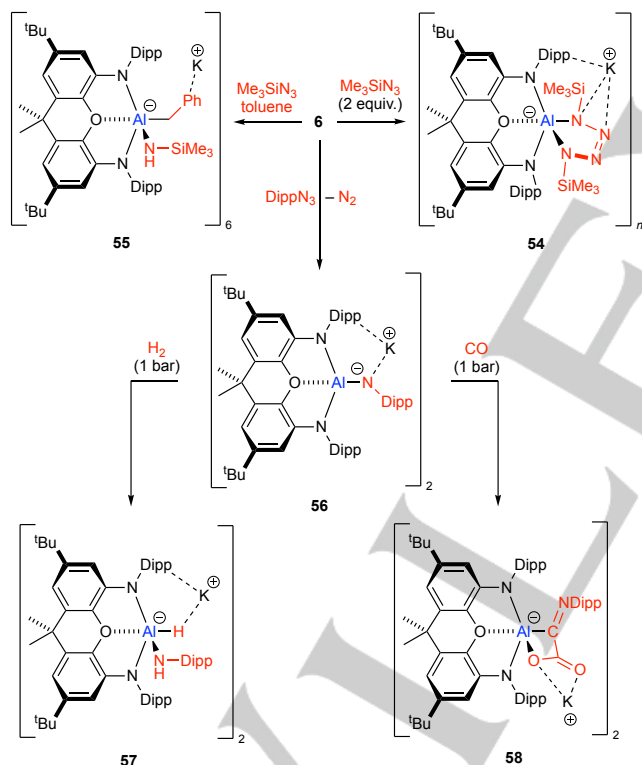
Scheme 9. Oxidation of **6** with organic azides and the activation of H₂ and CO by the aluminium imide **56**.

The Al imide **56** was found to be extremely reactive with regards to small molecule activation, showing reactivity towards H₂ and CO under mild reaction conditions.[39] The reaction between **56** and H₂ led to heterolytic cleavage of the H₂ molecule to give **57** (Scheme 9), whilst the reaction with CO saw the C–C coupling of two CO molecules to give an unprecedented Al bound [(DippN)CCO₂]²⁻ fragment **58**.

In a report by Anker and Coles, a similar aluminium imide **59** was reported by the reaction between **7** and MesN₃ (Scheme 10).[47] This complex was found to react with CO₂ (1 atm.) at RT in a (2+2) cycloaddition reaction to give the carbamate complex **60**.
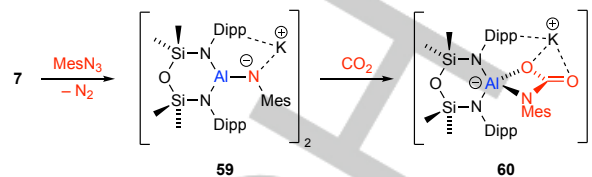
Scheme 10. Oxidation of **7** with MesN₃ to give the aluminium imide **59** and subsequent reactivity with CO₂.

3. Summary and Outlook

Although the field of aluminyl chemistry is still in its infancy, the scope of transformations reported by these novel anions is both fascinating and diverse. In this minireview, we have covered the synthesis, structures and reactivity for the currently known series of aluminyl anions. Reactions including nucleophilic substitution, oxidative addition, cycloaddition and oxidations have already been reported, with highlights including the facile C-H and C-F activation, small molecule activation and the ring opening of aromatics. DFT calculations performed on the series of known anions revealed some interesting trends with regards to their electronic structures. Firstly, anion **6** has the lowest energy LUMO+n (empty Al *p*-orbital) of the series in addition to one of the lowest HOMO-LUMO gaps. **6** is also one of only two anions (the second being **11**) that has been isolated free from its cation, which would otherwise stabilise the HOMO. These finding are consistent with its reactivity, as the monomeric anion **6** appears to be the most reactive of the current series (the only reported anion to ring open benzene for example). The diamido anions **7** and **8** have similar electronic structures, with **8** having a slightly smaller HOMO-LUMO gap due to a more destabilised HOMO. The alkyl systems **10** and **11** feature the high energy HOMOs as expected, due to the more electropositive substituents bound to the Al centre. **10** was found to have the smallest HOMO-LUMO gap of the series, but the charge-separated anion does not appear to be stable.

We believe the chemistry highlighted in this report only scratches the surface for what is to come from this novel class of nucleophiles. The coordination chemistry of the anions is only just beginning and small molecule activation including N₂ and CO is also yet to be reported. The use of aluminyl anions in catalysis is also an area that we are currently investigating. The field is rapidly expanding and definitely 'one to watch' over the next few years.

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MINIREVIEW

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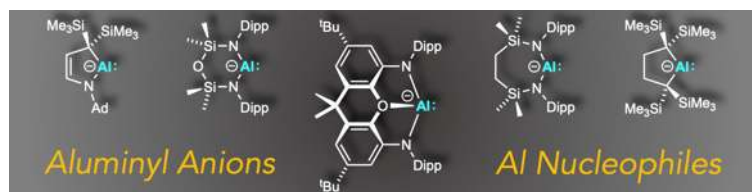
Nucleophilic Aluminium! A series of aluminium(I) anions (aka aluminyl anions) have recently been reported that remarkably show nucleophilic behaviour at aluminium. This minireview compares and contrasts the synthesis, structure, reactivity and electronic properties of these aluminyl anions whilst proposing future directions for the field.

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